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13. ABSTRACT *(Maximum 200 words)*

Air Force structures are susceptible to corrosion under normal service conditions. Many of these metallic and polymeric structures can be protected against corrosion by organic coatings. However, routine maintenance, special mission requirements, and the ever-increasing life-cycle requirements of these aircraft structures necessitate perio stripping of these coatings. The application, stripping, and disposal of these coatin cause a substantial environmental pollution problem for the Air Force. Current metal primers utilized by the US Air Force contain chromates to inhibit corrosion of the underlying metal. These chromates are both highly toxic and carcinogenic and pose a severe health risk to personnel involved in their application, stripping, and disposal The health risks are of particular concern during the stripping and disposal processes prior to refinishing the metal surfaces. Environmentally-friendly nonchromate replace ment primers have historically performed poorly with respect to corrosion inhibition. Microorganisms have been shown to both initiate and accelerate corrosion in many environments. The aim of this study was to investigate the interaction of chromates w microorganisms in an environment not traditionally associated with biologically-enhanc corrosion and to determine if the corrosion inhibiting action of the chromate pigment might be due, in part, to its action as a biocide. The results of this investigation provide some guidance in the search for envrionmentally-benign chromate replacements.

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FINAL TECHNICAL REPORT

For the Period of

March 1, 1995 to February 28, 1998

GRANT:

Biodegradation of Polymeric Coatings and Composites

GRANTEE:

University of Dayton Research Institute

300 College Park Avenue

Dayton OH 45469-0168

GRANT NO.:

F49620-95-1-0162

PRINCIPAL INVESTIGATOR:

Katie E. G. Thorp

OBJECTIVES

Air Force structures are susceptible to corrosion under normal service conditions. Many of these metallic and polymeric structures can be protected against corrosion by organic coatings. However, routine maintenance, special mission requirements, and the ever-increasing life-cycle requirements of these aircraft structures necessitate periodic stripping of these coatings. The application, stripping, and disposal of these coatings cause a substantial environmental pollution problem for the Air Force.

Current metal primers utilized by the US Air Force contain chromates to inhibit corrosion of the underlying metal. These chromates are both highly toxic and carcinogenic and pose a severe health risk to personnel involved in their application, stripping, and disposal. The health risks are of particular concern during the stripping and disposal processes prior to refinishing the metal surfaces. Environmentally-friendly nonchromate replacement primers have historically performed poorly with respect to corrosion inhibition.

Microorganisms have been shown to both initiate and accelerate corrosion in many environments. The aim of this study was to investigate the interaction of chromates with microorganisms in an environment not traditionally associated with biologically-enhanced corrosion and to determine if the corrosion inhibiting action of the chromate pigment might be due, in part, to its action as a biocide. The results of this investigation provide some guidance in the search for environmentally-benign chromate replacements.

STATUS OF EFFORT

The absence of chromate and the presence of biological activity can severely enhance the development of filiform corrosion. Aluminum panels which had been coated with a nonchromate primer were inoculated with a consortium of fungi and

bacteria prior to exposure to a salt fog and storage under humid conditions. This conditioning resulted in a significant growth of filiform corrosion around a scribe mark. The presence of chromate in the primer severely limited the formation of this corrosion. Likewise, in the absence of the inoculation procedure, the extent of corrosion was greatly diminished. These results suggested that the chromate acted as a biocide to limit corrosion which was enhanced by the presence of biological activity.

ACCOMPLISHMENTS / FINDINGS

Primers with and without chromium were required to investigate the premise that chromates act as a biocide to limit biologically-enhanced corrosion of a coated metal substrate. Two polyamide-based primers were obtained from DEFT, Inc. The primer compositions were essentially identical with the exception that one primer contained barium chromate as a corrosion inhibitor, while the other did not contain any corrosion inhibitor. The primers were prepared as directed by the manufacturer. Clad 7075 aluminum was the substrate used in this study, sectioned into panels measuring approximately 7.6 cm by 15.2 cm. Standard corrosion testing includes a chromate conversion coating on the substrate prior to application of the primer layer. However, while conversion coatings are usually applied to new structures, stripping and refinishing of existing structures are performed without the application of such a coating. Consequently, a conversion coating was not employed in the preparation of these test plates. An added advantage of this approach is the enhancement of corrosion without this protective coating, allowing comparisons of the various coating/environmental exposure combinations in a relatively short period of time.

The corrosion test matrix consisted of six combinations of the two primers (with and without chromium) and three conditioning environments (standard, sterile and inoculated with biological species), with six replicates for each combination. The

standard conditions included biological contamination experienced in normal handling procedures. The sterile conditions were obtained by immersing panels in a 70% solution of ethanol under ambient conditions for 30 minutes. For inoculation with biological species, panels were immersed for 30 seconds in a consortium of bacteria and fungi in malt broth.

The experimental conditions are identified in Table 1. Corrosion testing was performed in accordance with ASTM D2803-82 using Procedure A. Panel sets B and E were sterilized and sets C and F were inoculated with bacteria. All panels were then cleaned with an acid wash procedure, coated with the primer using a standard spray technique, and scribed with a diamond-tipped stylist. Panel sets B and E were sterilized again and sets C and F were inoculated again with bacteria. All panels were then exposed, in batches, to a salt fog for 24 hours and conditioned at 25°C and 85% relative humidity for 26 weeks in three separate chambers, corresponding to the three exposure environments.

TABLE 1. Test Matrix and Panel Identification for Corrosion Study

	Standard	Sterile	Inoculated
With chromate	A	B	C
Without chromate	D	E	F

Panels were periodically examined using a macro lens attached to a light microscope, and the extent of corrosion was documented with an image analysis system. After 26 weeks the panels were subjected to a tape-peel test, and the extent of coating peeled off due to poor adhesion was documented with the image analysis system. A sketch of the panel and the area analyzed for debonded coating is shown in Figure 1.

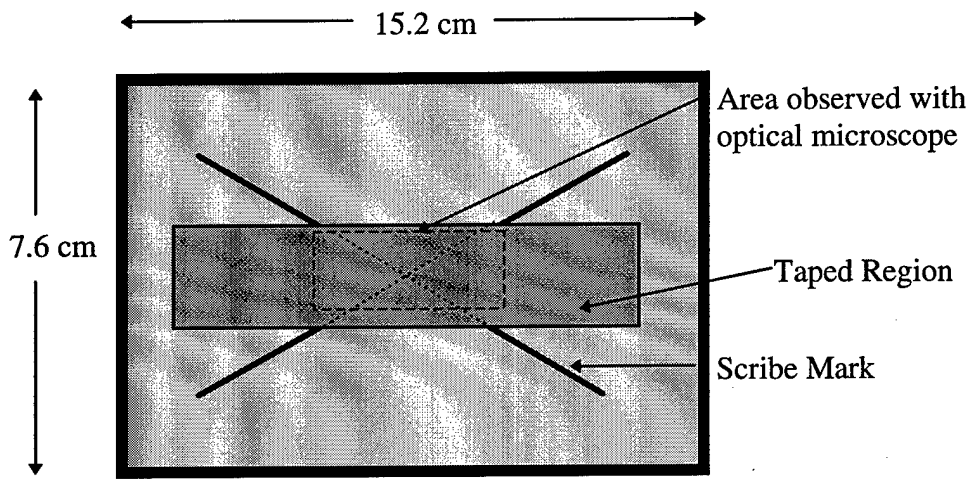
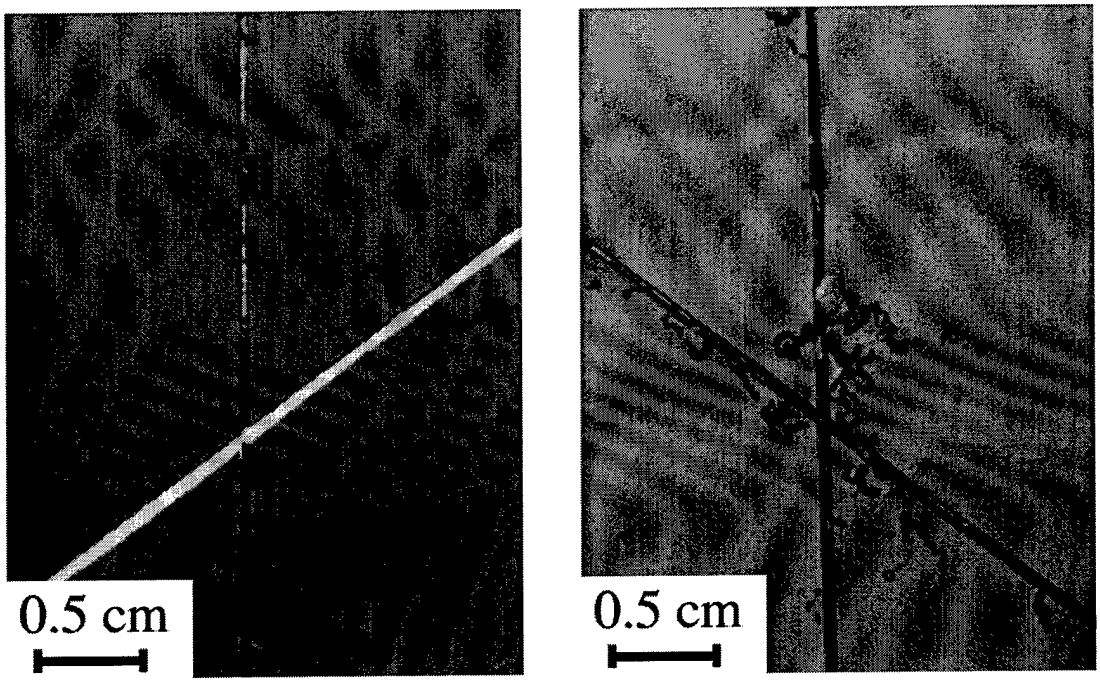


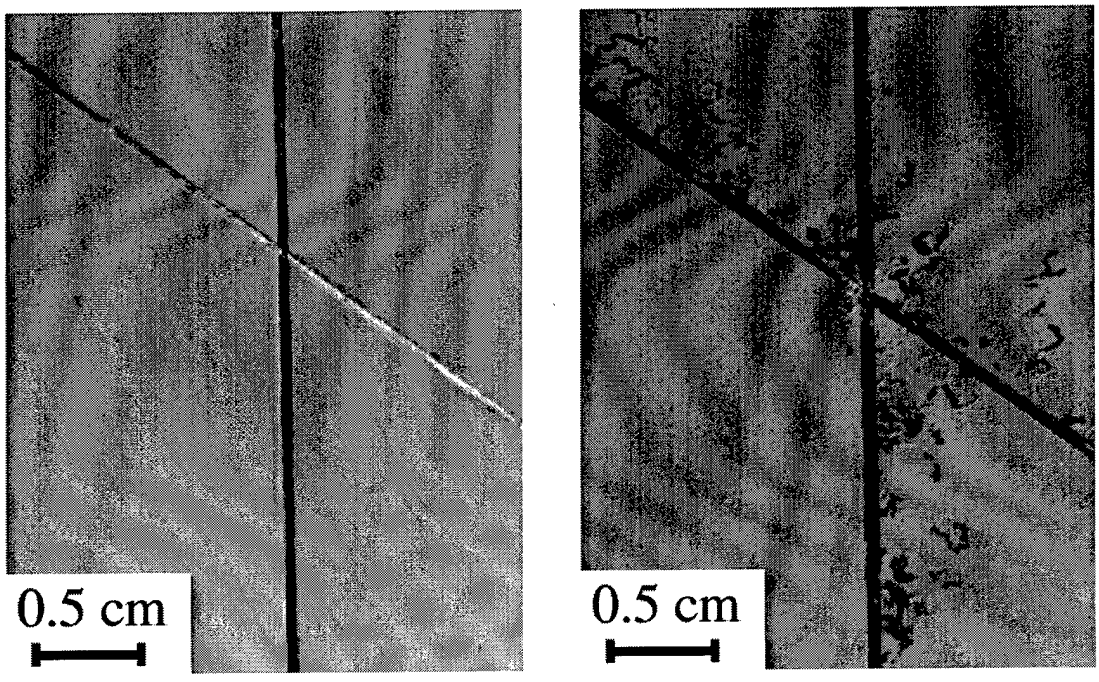
FIGURE 1: Sketch of panel and tape for peel test.

Prior to conducting the tape-peel test it was difficult to document visible differences in the extent of corrosion of the various panel sets. Filiform corrosion, as observed with the naked eye, appeared greatest in the panels of set F, but the difference between this and the other sets was not clearly apparent when viewed in the light microscope. The differences in corrosion between the various panel sets were clearly evident after the tape-peel test in which debonded or weakly-adhering primer was peeled off. Photographs of typical panel sections (in the vicinity where the scribes cross) are shown after the peel test in Figures 2-4. Panels from sets A, B and C showed little or no filiform corrosion, although some staining and corrosion were visible on the bare metal within the scribe marks. Panels from sets D, E and F all displayed evidence of corrosion, although the extent of corrosion varied with the conditioning environments. Panels from set F showed substantially greater corrosion than panels from sets D and E.



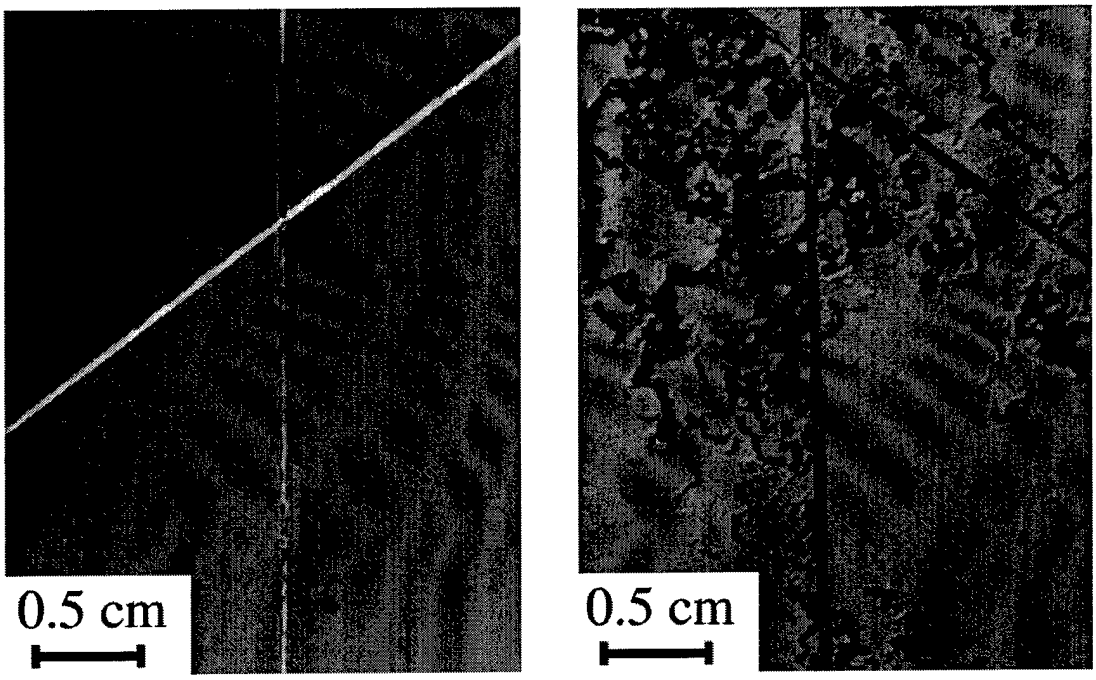
(a) (b)

FIGURE 2: Standard treatment panels (a) with chromate, set A, and (b) without chromate, set D.



(a) (b)

FIGURE 3: Sterilized panels (a) with chromate, set B, and (b) without chromate, set E.



(a) (b)

FIGURE 4: Inoculated panels (a) with chromate, set C, and (b) without chromate, set F.

The percent area of coating removed in the tape-peel test after 26 weeks of exposure is shown in Figure 5, in which the influences of primer composition and conditioning environment are evident. The addition of a chromate pigment clearly inhibited chemical corrosion as seen from a comparison of the results for the sterile environment. The sterile specimen without chromate in the primer (set E) had noticeably more corrosion than the sterile specimen with chromate in the primer (set B). Contact with biological activity associated with routine handling in the control group (sets A and D) did not appear to significantly enhance corrosion within the exposure period of this study. The results from that group were similar to those of the corresponding specimens in the sterile environment (sets B and E). The inoculated samples, however, displayed a significant increase in corrosion of the panels with the nonchromate primer as compared to panels with chromate in the coating. The relatively high extent of corrosion of the panels in this set (set F) was striking, considering the short immersion period in the inoculation medium (30 seconds on two occasions). The first inoculation period was followed by a standard acid wash which was probably sufficient to destroy any biological activity. Consequently, the critical treatment was probably the 30-second inoculation immediately preceding the salt fog exposure. These results suggested that biological

species contributed significantly to filiform corrosion, either directly or through enhancement of chemical corrosion.

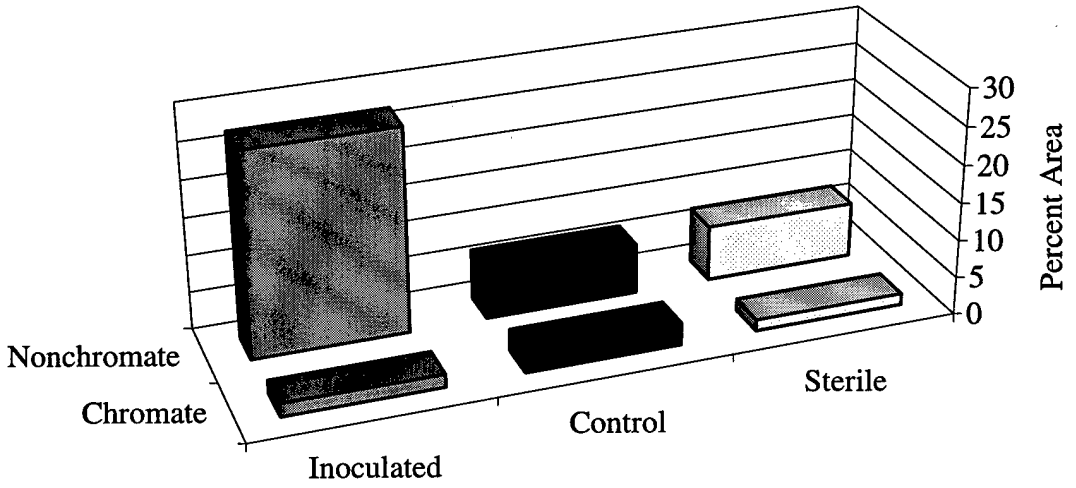


FIGURE 5: Percent area of primer removed as a result of the tape-peel test after 26 weeks.

The peeled area measured with the image analysis system for the chromate-containing primer specimens (sets A, B, and C) was primarily within the scribed regions of the samples and was not evidence of filiform corrosion. This area (1-3%) measured from the stained scribe region can be considered an indication of the minimum baseline signal measured from each panel. In essence, it represented a systemic error in the measurement technique. The amount of this signal (or error) was fairly consistent between exposure conditions and as a function of time. Therefore, it was not deemed necessary to develop an algorithm to correct for this consistent measurement error.

The lack of filiform corrosion on the panels coated with the chromate-containing primers can be explained by the biocidal character of the chromate. If the chromate acts to destroy the biological species which are present, then the inoculated chromate panels, in effect, are equivalent to the sterilized panels and display little or no corrosion as a result.

The effect of exposure condition for the nonchromate primer specimens (sets D, E, and F) is shown as a function of time in Figure 7. The rapid increase in the extent of corrosion in the inoculated nonchromate specimens was apparent. Very little difference was noticeable between the control and sterile specimens, suggesting possibly similar levels of biological activity in the control and sterile specimens, or contribution of a nonbiological process to the corrosion.

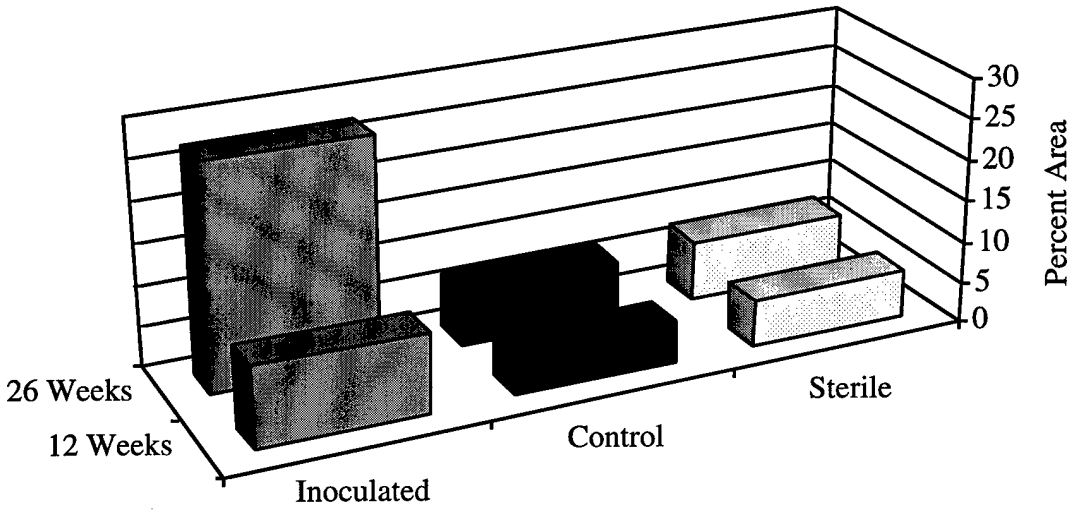


FIGURE 7: Percent area of nonchromate primer removed in the tape-peel test as a function of aging time.

The results reported here were limited to 26 weeks of environmental exposure. If, over time, the effectiveness of the chromate as a biocide is reduced or ceases (as suggested by the work of Mitchell, et al; at Harvard), then inoculated panels containing chromate pigments may begin to corrode as well, at a greater rate than panels not exposed to biological activity. The initial biocidal nature of the chromate, however, may be of extreme importance in inhibiting corrosion early in the life of a structure.

Specimens of the neat chromate and nonchromate primers were also cast and cut into small pieces. The pieces were then placed in a malt broth solution inoculated with common bacterial and fungal species. Periodically, specimens were removed and viewed under a scanning electron microscope to document the interaction of the biological species with the primers. The nonchromate primers appeared to be more heavily

colonized by the fungal species present in the solution. However, no physical degradation of either primer was noted.

The corrosion results obtained suggest that the absence of chromate and the presence of biological activity significantly enhance the development of filiform corrosion. In question, however, is whether filiform corrosion is a biologically or chemically driven process. One possible explanation for the above results was that the inoculation process exposed the panel to chemical species in the malt broth which enhanced corrosion of the panels. In addition the presence of corrosion on the sterile specimens and the similar corrosion levels in the sterile and standard specimens suggested that either the "sterile" specimens were not sterile, or biological activity was not critical for the filiform corrosion process. In order to address each of these issues, a new experimental procedure was adapted.

A new experimental chamber was designed to ensure that the sterilized panels would remain sterile. The panels were to remain sealed in the chamber to insure that environmental contaminants did not inadvertently get transferred to the specimens. In order to determine the effect of the malt broth on the corrosion process, all specimens were to be dipped in either a sterile or inoculated malt broth depending on their specific exposure requirements. The investigation was to include a chromate primer, a nonchromate noninhibited primer, and a nonchromate inhibited primer. In addition each of these primers was to be investigated with the addition of a biocide incorporated by the manufacturer specifically for this study. Delays in getting these primers manufactured prohibited the completion of this research activity during the time period of the grant. This research will be completed in a follow-on grant under the supervision of Dr. Kimberly Trick at the University of Dayton.

PERSONNEL SUPPORTED

Katie E. G. Thorp	Materials Research Engineer
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Kimberly Trick	Professor, Environmental Engineering Technology
William R. Ragland	Chief Chemical Technician
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PUBLICATIONS

Peer Reviewed

Gu, J.-D., C. Lu, K. Thorp, A. Crasto and R. Mitchell. (1996). Microbical Degradation of Fiber Reinforced Polymeric Materials. *Corrosion/96*, Paper No. 275, NACE International, Houston, TX.

Gu, J.-D., T. Ford, K. E. G. Thorp & R. Mitchell. (1996). Microbial Growth on Fiber Reinforced Composite Materials. *International Biodeterioration & Biodegradation Journal*, Vol. 39, pp. 197-204.

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Gu, J.-D., C. Lu, R. Mitchell, K. E. G. Thorp & A. S. Crasto. (1997). Fungal Degradation of Fiber-Reinforced Composite Materials. *Materials Performance*, Vol. 36, No. 3, pp. 37-42.

Gu, J.-D., C. Lu, K. E. G. Thorp, A. S. Crasto & R. Mitchell. (1997). Fiber-Reinforced Polymeric Composites are Susceptible to Microbial Degradation. *Journal of Industrial Microbiology & Biotechnology*, Vol. 18, pp. 364-369.

Non-Peer Reviewed

Thorp, K. E. G, A. S. Crasto, J.-D. Gu & R. Mitchell. (1997). Mechanisms of Biocorrosion. *Proceedings of the DARPA Coatings Conference, Nov 19-21, 1996.*

INTERACTIONS / TRANSITIONS

Researchers on this program coordinated all activities with the Laboratory of Microbial Ecology at Harvard University. This interaction ensured the use of appropriate methods and analysis techniques for dealing with the microbial species involved in this study. This interaction also allowed for the sharing of materials which greatly enhanced the validity of the research conducted in both laboratories. In addition, all research activities were reviewed by and coordinated with researchers at the Air Force Research Laboratory's Materials and Manufacturing Directorate to insure appropriate experimental conditions and corrosion testing.

NEW DISCOVERIES, INVENTIONS OR PATENT DISCLOSURES

None.

HONORS / AWARDS

None.